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**(54) MgB<sub>2</sub> SUPERCONDUCTIVE WIRE AND MANUFACTURING METHOD THEREFOR**

**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide an inexpensive MgB<sub>2</sub> superconductive wire without using expensive Ta and Nb inner tubes and a manufacturing method therefore.

SOLUTION: This MgB<sub>2</sub> superconductive wire is characterized in arranging one or two or more MgB<sub>2</sub> filaments in a matrix made of Cu or CuNi alloys. MgB<sub>2</sub> powder or MgB<sub>2</sub> powder green compact is prepared and is filled into a Cu tube or a CuNi alloys tube, and the MgB<sub>2</sub> filaments are obtained by performing sintered heat treatment for MgB<sub>2</sub> powder or MgB<sub>2</sub> powder green compact after the area.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a cheap MgB<sub>2</sub> superconductivity line and its manufacture method.

[0002]

[Description of the Prior Art] In recent years, compared with the metal system superconductivity line of the conventional NbTi alloy system or A15 type compound system, the new superconductor MgB<sub>2</sub> equipped with far high critical temperature (about 39 K) was discovered. However, since [ weak ] MgB<sub>2</sub> is lacking in processability, when manufacturing a superconductivity line, it is performed by the following methods. namely, the wire drawing put MgB<sub>2</sub> powder or MgB<sub>2</sub> green compact in a metallic conduit first, produce a billet, and according this to swaging or a dice -- or further, it carries out a roll pressure total, and reduction-of-area processing is carried out and it considers as a predetermined configuration Next, heat-treat, the filament which sintered MgB<sub>2</sub> powder inside a wire rod and continued is made to form, and, finally a MgB<sub>2</sub> superconductivity line is obtained.

[0003] Moreover, when obtaining a compound multicore line, two kinds of following methods are taken. First, the 1st method produces the compound rod which put MgB<sub>2</sub> powder or MgB<sub>2</sub> green compact in the metallic conduit, and carried out reduction-of-area processing, puts two or more [ the ] in a metallic conduit further, produces a compound multicore billet, and after it carries out reduction-of-area processing of this similarly, it performs sintering heat treatment. Moreover, as 2nd method, MgB<sub>2</sub> powder or MgB<sub>2</sub> green compact is put in a porous metallic conduit, a compound multicore billet is produced, and after carrying out reduction-of-area processing of this, sintering heat treatment is performed.

[0004]

[Problem(s) to be Solved by the Invention] With the conventional technology, the double pipe with which the metallic conduit has arranged the outer tube made from Cu or Cu alloy on the periphery of the product made from Ta or the inner tube made from Nb was used. Since each of these metals has good processability and is refractory metals, the reason Ta or Nb is used for an inner tube is for hardly reacting with MgB<sub>2</sub> at the time of sintering heat treatment. On the other hand, the reason Cu and Cu alloy are used for an outer tube is because it can be easy to process these, and the portion which cannot be touched can be replaced with MgB<sub>2</sub> to a cheap material and material cost can be lowered.

[0005] However, if Ta and Nb which are used as an inner tube of a metallic conduit are expensive, and thickness of an inner tube is made thin in order to reduce the amount used, its time and effort of light-gage processing will increase conversely, and they will become comparatively high-priced. That is, using Ta and the inner tube made from Nb itself had become the factor which pulls up the manufacturing cost of a MgB<sub>2</sub> compound superconductivity line.

[0006] In view of this situation, this invention was not made, as a result of inquiring wholeheartedly, and the purpose is in offering the cheap MgB<sub>2</sub> superconductivity line which uses neither expensive Ta nor the inner tube of Nb, and its manufacture method.

[0007]

[Means for Solving the Problem] In order to solve the aforementioned technical problem, the 1st mode of this invention is a MgB<sub>2</sub> superconductivity line characterized by being arranged in the matrix which 1 or two MgB<sub>2</sub> filaments or more become from Cu or a CuNi alloy.

[0008] The 2nd mode of this invention is the manufacture method of the MgB<sub>2</sub> superconductivity line characterized by preparing MgB<sub>2</sub> powder or MgB<sub>2</sub> green compact, stuffing Cu pipe or a CuNi alloy pipe, performing sintering heat treatment after carrying out reduction-of-area processing, and obtaining MgB<sub>2</sub> filament.

[0009]

[The form of operation] The form of operation of this invention is explained below. In this invention, MgB<sub>2</sub> powder or its green compact is directly put in Cu pipe or a CuNi alloy pipe, after carrying out reduction-of-area processing, sintering heat treatment can be performed and MgB<sub>2</sub> filament can be obtained. That is, the superconductor of the structure where MgB<sub>2</sub> filament has been arranged in the matrix of Cu or a CuNi alloy can be obtained.

[0010] The green compact of MgB<sub>2</sub> powder prepares what put MgB<sub>2</sub> powder in the container made of rubber, and was produced in the desired size by hydrostatic-pressure processing between the colds. next, the wire drawing put the green compact of MgB<sub>2</sub> powder or MgB<sub>2</sub> powder in a metallic conduit, produce a billet, and according this to swaging or a dice -- or further, it carries out a roll pressure total, and reduction-of-area processing is carried out and it considers as a predetermined configuration Moreover, in order to obtain a compound multicore line, a metallic conduit is compound \*\*\*\* stuffed [ which MgB<sub>2</sub> powder and the green compact were put in the metallic conduit, and carried out reduction-of-area processing ] further, or MgB<sub>2</sub> powder and two or more green compacts are put in a porous metallic conduit, it considers as a compound multicore billet, reduction-of-area processing of this is carried out similarly, and it considers as a predetermined configuration.

[0011] Next, the thing of a predetermined configuration performs sintering heat treatment. What is necessary is just to perform sintering heat treatment at 900 degrees C for example, in Ar gas atmosphere for 2 hours. In addition, as for heat treatment temperature, it is desirable that it is 1100 degrees C or less above 650 degrees C. If temperature is low, sintering [ of MgB<sub>2</sub> particles ] will become inadequate, and if temperature is high, in order for many of MgB(s)<sub>2</sub> to carry out composition change on the other hand MgB<sub>4</sub>, a transition-current value high in any case is not acquired.

[0012] It is desirable to use Cu or a CuNi alloy for the metal which touches MgB<sub>2</sub> with the form of this operation. The content of nickel can choose a CuNi alloy freely, after taking into consideration the mechanical strength of a metallic conduit, and the balance of a manufacturing cost.

[0013] The reason using Cu or a CuNi alloy is explained below. Since sintering heat treatment performed after \*\*\*\* processing was an elevated temperature, Cu and nickel dissolved to MgB<sub>2</sub> crystal lattice conventionally, the lattice constant changed, and it was thought that a superconductivity performance was spoiled. However, this invention person etc. discovered not producing such a dissolution phenomenon.

[0014] That is, about MgB<sub>2</sub>, if in contact with Cu or the CuNi alloy, some Mg will combine with Cu or nickel, and a Mg-Cu compound or a Mg-nickel compound will generate to a metallic-conduit side. Although it decomposes into the compound to high B concentration to MgB<sub>4</sub> or MgB<sub>7</sub>, the melting point is as high as the compound by the side of high B concentration, and it is hard coming to decompose MgB<sub>2</sub> from which Mg was taken. Therefore, the compound layer of high B concentration is thinly formed in the interface of the MgB<sub>2</sub> and the metallic conduit with which it filled up in the metallic conduit, and Mg diffusion to a metallic conduit is remarkably prevented from MgB<sub>2</sub>.

[0015] On the other hand, since Cu and nickel hardly dissolve to B or Mg, they do not make the MgB<sub>2</sub> crystal structure distorted. Of course, although the area of a superconductivity portion decreases strictly and a transition current falls in order for a part of periphery section (portion which touches a metallic conduit) of the MgB<sub>2</sub> restoration section to decompose into MgB<sub>4</sub> and

MgB<sub>7</sub> of the usual state electrical conduction matter, the degree of fall is not few, and it is satisfactory practically.

[0016] Moreover, a CuNi alloy is the range of total nickel concentration, and has the advantage in which processability is good. Therefore, nickel content of a CuNi alloy pipe can choose the mechanical strength and nickel of a metallic conduit freely, after taking the balance of a manufacturing cost into consideration, since it was a high price compared with Cu.

[0017] In addition, it is possible if it is the range to which independence or that more than one add also spoil a superconductivity property for Au, Ba, Be, Bi, C, calcium, Ce, Co, Cr, Fe, Gd, germanium, Hf, La, Ta, and Ti with the small solubility to B or Mg greatly neither in Cu nor a CuNi alloy pipe for the purpose of the grain-size-number adjustment and the improvement in a mechanical strength in a usual state electrical-conduction matrix. Furthermore, the method of making Cu and the CuNi alloy distribute a MgO particle is also effective in improvement in a mechanical strength. This [ MgO's ] is hard, and since the bonding strength of Mg and O is very strong, it is for heat treatment at the time of sintering not decomposing, and not polluting MgB<sub>2</sub> particle.

[Example] (Example 1) MgB<sub>2</sub> powder of 99% of purity was put in the container made of rubber, hydrostatic-pressure processing between the colds was carried out by the pressure of 100Mpa, and the green compact whose outer diameter is 9.8mm was produced. Next, after putting a green compact into Cu tube manufacturing whose outer diameter a bore is 10mm and is 14mm, the lid made from Cu was inserted in the ends of a pipe, electron beam welding of the insertion section was carried out in the vacuum, and the compound billet was produced. Next, after carrying out the reduction of area of the billet to the diameter of 1.0mm by swaging and the dice wire drawing, the roll pressure total was performed and the tape whose width of face thickness is 0.15mm and is 3.4mm was produced. Next, heat treatment was performed for this tape at 900 degrees C in Ar gas atmosphere for 2 hours. The tape cross section after heat treatment was shown in drawing 1. In drawing 1, a sign 1 is a MgB<sub>2</sub> sintering rod. Signs 2 are MgB<sub>4</sub> and a MgB<sub>7</sub> generation compound. A sign 3 is Cu pipe.

[0018] (Example 2) Using the metallic conduit as the CuNi (30wt%nickel) alloy, other conditions presupposed that it is the same as an example 1, and produced the tape whose width of face thickness is 0.15mm and is 3.4mm. Next, heat treatment was performed for this tape at 900 degrees C in Ar gas atmosphere for 2 hours. The tape cross section after heat treatment was \*\*2\*\* (ed). In drawing 2, a sign 1 is a MgB<sub>2</sub> sintering rod. Signs 2 are MgB<sub>4</sub> and a MgB<sub>7</sub> generation compound. A sign 5 is a CuNi (30wt%nickel) pipe.

[0019] (Example 3) The MgB<sub>2</sub>-Cu compound wire with a diameter [ before heat treatment used in the example 1 ] of 1.0mm was cut by fixed length, these seven were again packed into Cu pipe whose outer diameter a bore is 3.2mm and is 6mm, the lid made from Cu was inserted in ends, electron beam welding of the insertion section was carried out in the vacuum, and the compound multicore billet was produced. After carrying out the reduction of area of the billet to the diameter of 1.0mm by swaging and the dice wire drawing, the roll pressure total was performed and the tape whose width of face thickness is 0.15mm and is 3.4mm was produced. Next, heat treatment was performed for this tape at 900 degrees C in Ar gas atmosphere for 2 hours. The tape cross section after heat treatment was shown in drawing 3. In drawing 3, a sign 1 is a MgB<sub>2</sub> sintering rod. Signs 2 are MgB<sub>4</sub> and a MgB<sub>7</sub> generation compound. A sign 3 is Cu pipe. A sign 4 is Cu pipe containing what was shown with signs 1-3.

[0020] (Example 1 of comparison) Except the inner tube made from Nb whose outer diameter a bore is 10.0mm and is 10.6mm, and the bore having used the metallic conduit as the double pipe of the outer tube made from Cu 10.8mm and whose outer diameter are 14mm, processing conditions were made the same as an example 1, and the tape whose width of face thickness is 0.15mm and is 3.4mm was produced. Next, heat treatment was performed for this tape at 900 degrees C in Ar gas atmosphere for 2 hours. The tape cross section after heat treatment was shown in drawing 4. In drawing 4, a sign 1 is a MgB<sub>2</sub> sintering rod. A sign 6 is Nb pipe. A sign 3 is Cu pipe. A sign 3 is Cu pipe.

[0021] (Example 2 of comparison) After putting MgB2 green compact with outer diameter of 9.8mm in Nb tube manufacturing whose outer diameter a bore is 10mm and is 10.6mm, they were put into the outer tube made from Cu whose outer diameter a bore is 10.8mm and is 14mm, the lid made from Cu was inserted in ends, electron beam welding of the insertion section was carried out in the vacuum, and the compound billet was produced. After carrying out the reduction of area of the billet to the diameter of 1.0mm by swaging and the dice wire drawing, the compound wire was cut by fixed length, these seven were again packed into Cu tube manufacturing whose outer diameter a bore is 3.2mm and is 6mm, the lid made from Cu was inserted in ends, electron beam welding of the insertion section was carried out in the vacuum, and the compound multicore billet was produced.

[0022] After carrying out the reduction of area of the billet to the diameter of 1.0mm by swaging and the dice wire drawing, the roll pressure total was performed and the tape whose width of face thickness is 0.15mm and is 3.4mm was produced. Next, heat treatment was performed for this tape at 900 degrees C in Ar gas atmosphere for 2 hours. The tape cross section after heat treatment was shown in drawing 5. In drawing 5, a sign 1 is a MgB2 sintering rod. A sign 6 is Nb pipe. A sign 3 is Cu pipe. A sign 4 is Cu pipe containing what was shown with signs 1, 3, and 6.

[0023] About the heat treatment article of examples 1-3 and the examples 1-2 of comparison, the interface of a MgB2 sintering filament and a metallic conduit was observed. When the unusual appearance with a thickness of 0.5 micrometers was generating to the interface in the examples 1 and 3 using Cu pipe and having been analyzed, it was the mixture of MgB4 and MgB7. Moreover, in the example 2 using the CuNi (30wt%nickel) alloy, the unusual appearance with a thickness of about 0.3 micrometers was generating to the interface, and when it was analyzed, MgB4, MgB7, and nickel of a minute amount were detected. On the other hand, the unusual appearance was not detected by the interface of MgB2 and Nb pipe in the example of comparison using Nb inner tube.

[0024] The sample was taken from three places about the heat treatment article of examples 1-3 and the examples 1-2 of comparison, and transition-current measurement by 4 terminal method was performed in liquid helium. On the other hand, the cross-section photograph of each sample after heat treatment was taken, and the area of portions other than a metallic conduit was computed. The critical current density (it is called Following  $J_c$ ) of portions other than a metallic conduit was computed by having broken the acquired transition-current value by area of portions other than a metallic conduit. The result was shown in Table 1 as drawing 6.

[0025] There is almost no difference of  $J_c$  of the examples 1 and 2 of this invention and  $J_c$  of the example 1 of comparison, and, similarly the difference of  $J_c$  of the example 3 of this invention and  $J_c$  of the example 2 of comparison does not almost have comparison of multicore lines at single fiber lines so that clearly from Table 1. Therefore, according to this invention, it becomes possible to acquire an equivalent superconductivity property, without using large sum Ta pipe and Nb pipe.

[0026] [Effect of the Invention] According to the manufacture method of the MgB2 superconductivity line of this invention, the MgB2 superconductivity line of the outstanding property is efficiently producible. Therefore, the contribution on industry is remarkable.

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